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Effects of broadleaf woodland cover on streamwater chemistry and risk assessments of streamwater acidification in acid-sensitive catchments in the UK

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Abstract

Streamwater was sampled at high flows from 14 catchments with different (0-78%) percentages of broadleaf woodland cover in acid-sensitive areas in the UK to investigate whether woodland cover affects streamwater acidification. Significant positive correlations were found between broadleaf woodland cover and streamwater NO_3 and Al concentrations. Streamwater NO_3 concentrations exceeded non-marine SO_4 in three catchments with broadleaf woodland cover $\geq$ 50% indicating that NO_3 was the principal excess acidifying ion in the catchments dominated by woodland. Comparison of calculated streamwater critical loads with acid deposition totals showed that 11 of the study catchments were not subject to acidification by acidic deposition. Critical loads were exceeded in three catchments, two of which were due to high NO_3 concentrations in drainage from areas with large proportions of broadleaved woodland. The results suggest that the current risk assessment methodology should protect acid-sensitive catchments from potential acidification associated with broadleaf woodland expansion.

Capsule:

Broadleaf woodland <30% of catchment area should not pose a risk of increased streamwater nitrate and aluminium concentrations within acid-sensitive catchments.

Keywords: broadleaf woodland; critical loads; Forests & Water Guidelines; streamwater acidification

1. Introduction

Conifer afforestation has been associated with elevated streamwater acidity and aluminium concentrations (Ormerod et al., 1989) and contributing to the decline or complete loss of fish populations and other freshwater biota in acid-sensitive areas of the UK (Harriman et al., 1987). Forests contribute to surface water acidification in areas of high acid deposition due to the enhanced canopy capture of atmospheric pollutants ('the scavenging effect') (Nisbet et al., 1995), especially by dry and occult deposition, as a result of increased turbulent air mixing (Fowler et al., 1989). Another factor is the accumulation and removal of base cations in harvested trees. Areas most affected by acidification have soils with small exchangeable base cation pools which are rapidly depleted in response to acidic deposition, resulting in the acidification of soils and freshwaters. Reducing emissions of acid pollutants has been recognised as the principal way of solving the problem of acidification. In the UK, it is estimated that sulphur (S) and nitrogen (N) emissions declined by 71% and 35%, respectively, between 1986 and 2001, while deposition of non-marine S declined by 60% over the same period (Fowler et al., 2005). Future reductions in S and N emissions have been determined by the Gothenburg Protocol, under the UNECE Convention on Long-Range Transboundary Air Pollution, which aims to facilitate the recovery of acidified terrestrial and aquatic ecosystems (Jenkins and Cullen, 2001). In the UK, this will involve reductions from 1990 levels of around 80% in S and 45% and 20% in oxidised and reduced N emissions, respectively, by 2010 (NEGTAP, 2001).

Despite the decline in emissions of acid pollutants and in conifer afforestation in the UK since the 1980s, there is concern that increasing forest cover from the expansion of broadleaf woodlands could delay the recovery of acidified surface waters, or even lead to further acidification, in the most sensitive areas. Planting of broadleaves has gradually increased since the 1970s, with more than 11 000 ha planted in the UK in 2005, as the result of policies and initiatives to restore native broadleaf woodlands and improve the conservation status and habitat value of forested ecosystems (Rollinson, 2000). Although pollutant deposition is less on broadleaf woodland than on the more aerodynamically rough conifer canopies (Robertson et al., 2000), large-scale broadleaf planting schemes may still exert a significant impact on the most acid-sensitive freshwaters where critical loads are likely to remain exceeded (Alexander and Cresser, 1995).

This study aimed to: 1) determine if there is an association between the proportion of broadleaf woodland cover within acid-sensitive catchments and various indicators of water acidification and; 2) assess the effectiveness of the critical loads methodology for identifying catchments at risk of acidification where broadleaf woodland is expanding.

2. Assessing the risk of freshwater acidification using the critical loads methodology

The critical loads methodology is used for assessing and mapping freshwater acid-sensitivity in 24 countries in Europe and North America (UBA, 2004). It has been incorporated into the Forests & Water Guidelines (Forestry Commission, 2003) which describe best practice for minimising the effect of forestry activities on the freshwater environment in the UK. The Guidelines use the provisional critical loads exceedance map for UK freshwaters shown in Fig. 1 to determine freshwaters at risk of acidification from the scavenging effect due to new woodland planting or restocking plans in acid-sensitive areas. The map was derived from calculating critical loads with the Steady-State Water Chemistry (SSWC) model (Henriksen et al., 1986) from the chemical analysis of water samples from the most sensitive water body, usually a lake, within each 10 km x 10 km grid square. These were then compared with the modelled atmospheric deposition of non-marine S and N for 1995-1997. When more than 10% of a catchment area is to be planted with conifers or more than 30% with broadleaves within a critical load exceedance square (i.e., in which modelled deposition exceeds the critical load value), or adjacent square, the Guidelines require a site-specific critical load assessment. This involves the chemical analysis of one to three water samples collected from the catchment outlet at high flows, preferably from January to March, when streamwater tends to be more acidic. Where the estimated pollutant deposition exceeds the critical load calculated for the specific catchment, approval of a planting grant or restocking plan is unlikely until pollutant emissions are reduced.

Figure 1

3. Materials and methods

3.1. Catchment selection

Catchments selected for the study lay within acid-sensitive areas of the UK and ranged in percentage cover of broadleaf woodland with no other confounding land uses. Study catchments were identified and characterised using digital spatial datasets in an ArcGIS (ESRI, CA, USA) Geographical Information System (GIS). The critical loads exceedance dataset utilised by the Forests & Water Guidelines (ECRC, 2001, 10 km grid) and the National Inventory of Woodlands and Trees-Interpreted Forest Type (Forestry Commission, 1:25 000) were used to select broadleaf woodland polygons lying within, or adjacent to, a critical load exceedance square. Catchment areas were delineated from digital elevation models (Ordnance Survey/EDINA, Land-Form PROFILE®, 1:10 000) and percentages of broadleaf woodland cover were calculated in each catchment. The underlying geology was determined from a digital 1:625 000 scale geology map (BGS, 1995) and the proportions of soil types calculated from the digital 1:250 000 scale National Soil Maps for England and Wales (NSRI, 1984) and for Scotland (MISR, 1981).

3.2. Catchment description

Following field visits, 10 forested catchments representative of acid-sensitive areas throughout the UK were selected in Scotland (Glen Arnisdale, three catchments and the Loch Katrine area, four catchments) and England (two catchments near Ullswater in north-west England and the Yarner Wood catchment in Devon, south-west England) (Fig. 1). Three control catchments with no woodland cover were also selected, one adjacent to each group of catchments in Glen Arnisdale, and the Loch Katrine and Ullswater areas. The control for the Yarner Wood catchment was the nearby (20 km) Narrator Brook catchment, which had only 2% broadleaf woodland cover and is part of the UK Acid Waters Monitoring Network (AWMN, Evans et al., 2000).

The characteristics of the study catchments are summarised in Table 1 and detailed in Gagkas (2007). Catchment geologies and soils were mainly acid-sensitive. Broadleaf woodland covered from 10.3% to 78.7% of the forested catchments. Woodlands were dominated by open canopy, natural downy birch (*Betula pubescens*) in the Scottish catchments and by mature, semi-natural alder (*Alnus glutinosa*) and semi-natural and ancient sessile oak (*Quercus petraea*) in the Ullswater area and Yarner Wood catchments, respectively. The Scottish control catchments were covered by acid grassland and blanket bog, dominated by ericoid shrubs and grasses in Glen Arnisdale and by purple moor grass (*Molinia caerulea*) and patches of fen in the Loch Katrine area. The Ullswater area control catchment was covered by wet heath and fen communities and Narrator Brook by acid grassland and blanket bog dominated by *Molinia caerulea*. Catchments in Glen Arnisdale and the Loch Katrine area had an upland character while those near Ullswater and in Devon had a gentler relief and lower altitudes. Catchment distance from the nearest coast ranged from 2 km (Glen Arnisdale) to 57 km (Loch Katrine area). Mean annual rainfall, calculated from rainfall records spanning 29 to 37 years, ranged from 1010 mm (Ullswater area) to 2275 mm (Loch Katrine area) (British Atmospheric Data Centre, BADC).

Table 1

3.3. Streamwater sampling and chemical analysis

Two to 10 streamwater samples were collected at the catchment outlets from January to April 2005 and November 2005 to March 2006 during high flow conditions. All streamwater samples were taken in acid-washed polyethylene bottles and stored in the dark at 4 °C prior to analysis at Edinburgh. Gran alkalinity was determined within 48 hours of sample collection by manual titration with 0.01 M HCl from pH 4.5 to 3.5 (Neal, 2001). Ca, Mg, Na and K were determined using a Unicam AA M Series flame atomic absorption spectrometer, Cl and SO_4 with a Dionex DX-500 liquid chromatography system and NO_3 with a Bran & Luebbe AA3 continuous flow analyser. Al was determined as total filtrable Al using a Perkin Elmer Optima 5300 inductively coupled plasma-optical emission spectrometer in water samples that had been passed through 0.45 μm cellulose nitrate membrane filters after collection and then acidified with 2 ml concentrated HNO_3 l^{-1} to minimise loss through adsorption to the bottle and precipitation. Standard laboratory quality assurance measures detailed in Gagkas (2007) provided confidence in the accuracy, precision and reproducibility of the streamwater analyses. Streamwater chemistry data for three samples from Narrator Brook were obtained for January-March 2005 from the AWMN to compare as a control with samples from the Yarner Wood catchment.

3.4. Calculation of critical loads and exceedences

Non-marine solute concentrations were calculated using published seasalt correction factors (UBA, 2004). Streamwater acid neutralising capacity (ANC) was determined in μeq l^{-1} as the difference between the measured streamwater base cation (Ca, Mg, Na, K) and acid anion (Cl, SO_4, NO_3) concentrations. Critical loads and exceedances were calculated according to the methodology of the Forests & Water Guidelines since this is the risk assessment approach currently used, even though alternative methods and new deposition data are available (UK National Focal Centre, 2004). Mean high flow streamwater chemistry was used in the SSWC model to calculate the critical loads (CL) for each catchment (Equation 1). CLs are based on the principle that the acid load to water should not exceed the long-term supply of neutralising base cations in the catchment, represented by the pre-industrial concentration of non-marine base cations ($[BC_0^*]$) derived from weathering minus a critical buffer concentration, as shown in Equation 1 (Henriksen et al., 1986),

$$CL = \left([BC_0^*] - [ANC_{crit}]\right) \cdot Q \qquad \text{(Equation 1)}$$

where ANC_{crit} is the lowest concentration that does not damage selected biota. The Guidelines use a value of $ANC_{crit} = 0$ μeq l^{-1}, which provides a 50% probability of brown trout (*Salmo trutta*) populations being protected based on mean chemistry (UK National Focal Centre, 2004), but is thought to provide complete protection at high flows. Catchment runoff (Q), calculated as 85% of the catchment annual rainfall, is used to convert concentrations to fluxes.

CL exceedance was calculated by comparing CL values with the estimated deposition of non-marine S (S_{dep}) and N (Equation 2),

$$Exceedance = \left(S_{dep} + \left(NO_3 \cdot Q\right)\right) - CL \qquad \text{(Equation 2)}$$

N deposition was estimated for each catchment as the mean streamwater NO_3-N concentration measured at high flow converted to a flux using rainfall data for 2005 provided by the BADC. Two estimates of non-marine S deposition were used: a) modelled data for 1995-97 as recommended by the Forests & Water Guidelines and b) the most recent (2002) data generated by the FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) model (Singles et al., 1998).

4. Results

4.1. Streamwater chemistry

The streamwater chemistry results for the study catchments are summarised in Table 2. Mean high flow alkalinity in 12 catchments ranged from -35.3 to 41.6 μeq l^{-1}, and was 141 μeq l^{-1} in ULCON. Streamwater in these catchments was therefore considered strongly and moderately acidic, respectively, in comparison with Neal's (2001) definition of waters with alkalinity < 200 μeq l^{-1} as acidic. Catchment UL2 had a higher mean streamwater alkalinity (278 μeq l^{-1}) and appeared to be well buffered to acidic inputs, perhaps due to local outcrops of more base-rich geology. The acid-sensitive nature of the catchments, with the exception of UL2, is indicated by the negative and small positive mean streamwater ANC values. Mean streamwater concentrations of marine SO_4 and non-marine SO_4 (xSO_4) ranged from 34.4 to 101 μeq l^{-1} and 10.9 to 72.4 μeq l^{-1}, respectively, with the higher concentrations measured in the English catchments. The highest mean streamwater NO_3 concentrations were in the three forested English catchments and ranged from 41.4 to 107 μeq l^{-1}, with the greatest values in the forested Ullswater catchments (maximum concentration of 179 μeq l^{-1} in UL1). Mean NO_3 concentrations were generally lower in the nine Scottish catchments and in the two English control catchments, ranging from 3.40 to 11.4 μeq l^{-1}. Mean streamwater Al concentrations were highest in catchment UL1 (3.27 μmol l^{-1}), while the lowest concentrations occurred in the Ullswater control catchment and some of the Loch Katrine area catchments. Calculated Na:Cl ratios in streamwater for many of the study catchments were close to the value for seawater of 0.86, indicating that seasalt inputs accounted for most of the Na in winter high flow samples. The maritime influence on streamwater chemistry was greatest in the Glen Arnisdale catchments (Na:Cl ratios in streamwater of 0.63-0.71), and least in LKCON, UL2 and ULCON (Na:Cl ratios in streamwater of 0.97-1.12).

Table 2

4.2. Effect of broadleaf woodland cover and other catchment characteristics on streamwater chemistry

Relationships between mean streamwater solute concentrations and catchment characteristics (percentage broadleaf woodland cover and percentage of gleysols and podzols) were investigated using correlation analysis (Spearman's rank) (Table 3). As expected there were significant positive correlations between mean streamwater Gran alkalinity and Ca and between the marine-derived ions, Na and Cl. The other atmospherically-derived ions, Mg and $SO_{4,}$ were also significantly positively correlated with Na and Cl and all marine-derived ions were significantly negatively correlated with distance from the nearest coast. Gran alkalinity and Al were significantly negatively correlated indicating a greater occurrence of Al in poorly buffered waters. The percentage of gleysols was significantly positively correlated with Ca, Mg and Na. However, this relationship was not significant for non-marine Mg and Na concentrations (r_s = 0.40, P>0.05 and r_s = -0.27, P>0.05, respectively), suggesting that the presence of gleysols in the study catchments provides buffering mainly through release of Ca. Significant negative correlations occurred between the percentage area of podzolic soils in a catchment and Ca, Mg, non-marine Mg (r_s = -0.51, P<0.05) and SO_4 (r_s = -0.51, P<0.05), the latter suggesting SO_4 retention by podzolic soils.

Table 3

Percentage broadleaf woodland cover was significantly positively correlated with mean streamwater NO_3 (Fig. 2a) and Al concentrations (Fig. 2b). Catchments with percentage broadleaf woodland cover less than 30% had mean streamwater NO_3 concentrations below 11.5 μeq l^{-1} , while the more heavily forested catchments YAR, UL1 and UL2 had the highest NO_3 concentrations. A significant positive correlation (r_s = 0.82, P<0.001) also occurred between percentage broadleaf woodland cover and the nitrate index, the ratio of NO_3:($x SO_4$ + NO_3) when expressed in μeq l^{-1} (Fig. 2c). The ratio provides an index of the influence of NO_3 on acidification status, assuming that both anions are derived from anthropogenic acid deposition (Curtis et al., 2005). Values above 0.5 indicate that NO_3 has a greater influence than $x SO_4$ on surface water acidification. Catchments with the highest percentage broadleaf woodland cover, YAR, UL1 and UL2, had the highest ratio values (0.48, 0.56 and 0.57, respectively, calculated as the mean values of water samples). There were no significant correlations between percentage broadleaf woodland cover and mean streamwater Cl and SO_4 (r_s = 0.28 and r_s = 0.29, respectively).

Figure 2

4.3 Critical loads and exceedance

CL values ranged from 0.40 to 2.64 keq H ha^{-1} yr^{-1}, showing moderate to high catchment susceptibility to acidification (Fig. 3). Using the modelled S deposition data for 1995-97 and estimated N deposition, CLs were found to be exceeded in three catchments, NAR, YAR and UL1 by 0.45, 0.81 and 1.74 keq H ha^{-1} yr^{-1}, respectively. NAR remained in the same CL exceedance class as its grid square, while YAR fell into a higher exceedance class and UL1 into the highest exceedance class (>1 keq H ha^{-1} yr^{-1}), despite lying in a not exceeded square (Table 1). CLs were not exceeded in the other catchments by 0.15 to 1.21 keq H ha^{-1} yr^{-1}. Compared to the provisional critical loads exceedance map, streamwater CLs were not exceeded in the Glen Arnisdale and Loch Katrine area catchments while non-exceedance remained in catchments UL2 and ULCON. When estimates of S deposition from the FRAME model for 2002 were used in the calculations, CLs were still exceeded in the same three catchments as previously in NAR, YAR and UL1 by 0.01, 0.36 and 1.02 keq H ha^{-1} yr^{-1}, respectively, even though the deposition estimates were lower than for 1995-1997. The amount by which CLs were not exceeded in the other catchments increased, with non-exceedance values ranging from 0.90 to 1.96 keq H ha^{-1} yr^{-1} (Fig. 3). In the catchments in which CLs were exceeded, NAR, YAR and UL1, mean high flow streamwater ANC was below 0 μeq l^{-1} (-19.2, -32.9 and -76.1 μeq l^{-1}, respectively), whilst in the Loch Katrine and Ullswater area catchments (UL2 and ULCON) in which CLs were not exceeded mean ANC ranged from 36.1 to 248 μeq l^{-1}. However, despite non-exceedance of CLs, catchments GA1, GA3 and GACON had negative mean high flow ANCs (-16.6, -32.3 and -13.2 μeq l^{-1}, respectively), and only GA2 had positive mean streamwater ANC (10.0 μeq l^{-1}).

Figure 3

5. Discussion

5.1. Factors controlling streamwater chemistry in the study catchments

There was clear evidence of an effect of broadleaf woodland cover on high flow streamwater chemistry in the study catchments since NO_3 and Al concentrations increased with % broadleaf woodland, despite significant variation in soil types and local pollutant deposition climate due to different distances from major pollutant sources. The catchments near Ullswater have been most impacted by acid deposition and lie within areas that received the highest measured deposition rates in the UK of 25 kg non-marine S and 25 kg total N ha^{-1} yr^{-1} in 1997 (NEGTAP, 2001). On the other hand the remote Glen Arnisdale catchments in north-west Scotland have never experienced large amounts of anthropogenic pollutant deposition and the acid sensitivity of freshwaters in this area is mainly due to the low buffering capacity of soils for acidic inputs (Harriman et al., 2001). The pollution climate in the Loch Katrine area and Devon is intermediate between these two extremes.

Wet S deposition dominated the modelled total non-marine deposition inputs to all the study catchments. This may explain the similar streamwater SO_4 and xSO_4 concentrations in the forested and unforested catchments in most of the study areas since the scavenging effect of forest canopies mainly enhances dry and occult deposition of pollutants. Streamwater SO_4 concentrations in the Devon and Loch Katrine area catchments could also have been influenced by SO_4 retention in the Feand Al-rich horizons of the dominant podzolic soils (Barton et al., 1999). Streamwater Cl concentrations appeared to be influenced more by distance from the nearest coast than by woodland scavenging in the Glen Arnisdale and Loch Katrine area catchments, where there was no significant difference in Cl concentrations between forested (10 to 30% cover) and unforested catchments. Only in the two catchments with high percentage woodland cover near Ullswater was there evidence of enhanced Cl capture by the woodland canopy, with mean Cl streamwater concentrations significantly greater than those in the control catchment ($P<0.05$, Kruskal-Wallis and non-parametric multiple comparison tests). Streamwater Ca and Mg concentrations appeared to be influenced by soil type and were generally higher in catchments with substantial percentages of gleysols (UL1, UL2 and Glen Arnisdale catchments) indicating possible contributions of Ca-rich water at depth even at high flows (Stevens et al., 1997).

5.2. Nitrate

The association between mean high flow streamwater NO_3 concentrations and percentage woodland cover indicated a “threshold” effect in which concentrations in the three heavily forested catchments (> 50% cover) were substantially higher than in catchments with woodland cover below 30%. The high streamwater NO_3 concentrations in catchments YAR, UL1 and UL2 can be attributed to the high local N deposition inputs, enhanced by the scavenging effect of the trees and the type and extent of broadleaf woodland cover, leading to increased soil acidification and N leaching. N deposition remains relatively high in north-west and south-west England due to proximity to pollution sources such as nitrous oxides from industry and transport and ammonia emissions from livestock agriculture. Pollutant scavenging increases with the height and density of the woodland canopy, especially for dry and occult deposition (Nisbet et al., 1995). The higher aerodynamic roughness of the dense oak and alder woodlands in the YAR, UL1 and UL2 catchments is expected to result in greater pollutant scavenging than the more open canopy of the birchwoods in the Glen Arnisdale and Loch Katrine area catchments. Furthermore, the positive association reported between NO_3 in streamwater and forest age in monoculture Sitka spruce plantations in Wales (Stevens et al., 1994) suggests that the mature woodlands in the YAR, UL1 and UL2 catchments may release more NO_3 into streamwater than the birchwoods in the Scottish catchments where succession has probably been arrested due to the harsher climate and grazing by animals. The higher streamwater NO_3 concentrations in catchments UL1 and UL2 may also be influenced by enhanced N leaching resulting from symbiotic N fixation in the alder-dominated woodland (Verburg et al., 2001).

The strong relationship between percentage broadleaf woodland cover and streamwater NO_3 index values indicates the important role of NO_3 in streamwater chemistry in heavily wooded catchments subject to high N deposition. NO_3 is the dominant excess acid anion in streamwater from catchments UL1 and UL2 and almost of equal importance to xSO_4 in YAR. Concentrations of reduced and oxidised N in rainfall currently exceed the non-marine S concentration by a factor of two in the UK (NEGTAP, 2001) and it is expected that the relative role of NO_3 in excess anion loads will probably increase in the future as xSO_4 concentrations continue to decline. Therefore, it has been suggested that NO_3 leaching could impede the recovery of acidified freshwaters in the UK uplands (Curtis et al., 2005).

5.3 Aluminium

Measured streamwater alkalinity at high flow indicated that all study catchments, apart from UL2, were acid-sensitive as a result of the base-poor, slowly weathering soil parent materials present. If UL2 is excluded from Fig. 2b, due to greater buffering in this catchment, there is an even stronger association between Al and % woodland cover, with $r_s = 0.83$ ($P<0.001$). The significant positive association between streamwater Al concentrations and percentage woodland cover can be attributed to the enhanced deposition of mainly N on woodland canopies and also NO_3 leaching from mature woodland stands, probably enhanced by the alder woodland in UL1. Both these processes cause Al displacement from the soil ion-exchange complex and subsequent leaching to streamwater. However, the toxicity of the increased Al concentrations in streamwater will depend on how much is present in the inorganic form (Lange et al., 2006).

5.*4. CL exceedance*

CLs were not exceeded in most of the study catchments by the modelled deposition inputs for both 1995-97 and 2002. Modelled deposition was lower, and consequently non-exceedance of CLs was higher, with the 2002 dataset due to marked reductions in S emission, and subsequent deposition, as a result of international agreements. Long term trends in streamwater $x\mathrm{SO}_4$ in AWMN catchments indicate that as levels of atmospherically deposited S have declined, surface water concentrations of $x\mathrm{SO}_4$ have fallen accordingly (Davies et al., 2005). However, despite the decline of inland sources of SO_2, S emissions from shipping have increased and become a significant contributor to S deposition in western coastal areas, such as south-west England (Fowler et al., 2005). This could help to explain the relatively high $x\mathrm{SO_4}$ streamwater concentrations and CL exceedance in the YAR and NAR catchments. Small increases in N deposition have also been reported in western areas, although total N deposition in the UK has remained fairly constant. The high CL exceedance in catchment UL1 was probably due to a combination of low soil buffering capacity and relatively high S and N deposition, possibly coupled with high N leaching to streamwater caused by N fixing by alder. The fact that the UL1 catchment was assessed as highly acid-sensitive, despite lying within a not exceeded square, shows the high variability in freshwater chemistry present within each 10 km^2 critical load square and the necessity for also conducting streamwater assessments for woodland expansion plans in areas adjacent to exceeded squares, as recommended in the Forests & Water Guidelines. The Loch Katrine area catchments received high S and N loadings, predominantly as wet deposition, but streamwater concentrations of SO_4, $x\mathrm{SO_4}$ and NO_3 were relatively low probably due to dilution by high rainfall amounts and/or SO_4 retention by catchment soils. Thus, in these catchments, the calculated CL values exceeded the acid deposition load and positive values of streamwater ANC were maintained (Table 2). Pollutant deposition in the remote Glen Arnisdale catchments was very low and consequently CLs were not exceeded. However, mean high flow streamwater ANC was negative for three of the four catchments (Table 2), mainly due to high excess Cl concentrations arising from seasalt-soil interactions. Non-exceedance of CLs resulted largely from the low calculated non-marine SO_4 concentrations, probably due to selective retention of pollutant SO_4 in seasalt-conditioned catchment soils (Harriman et al., 1995). The SSWC model is known to have difficulty in dealing satisfactorily with streamwater chemistry influenced by high seasalt inputs, especially during storm events (Battarbee, 1992). The three forested Glen Arnisdale catchments are probably naturally acid-sensitive, with episodic streamwater acidity driven by soil ion-exchange and the release of organic acids during seasalt events, potentially having an adverse impact on freshwater biota (Larssen and Holme, 2006).

6. Conclusions

Broadleaf woodland appears to exert a significant influence on streamwater chemistry in acid-sensitive catchments, mainly due to pollutant scavenging and NO_3 leaching, but only when woodland covers a large proportion) of the catchment area. Critical loads were not exceeded in most of the study catchments but atmospheric N deposition is of concern in those with very poor buffering and high woodland cover, where NO_3 was the principal acidifying ion and contributed to critical load exceedance. Almost all study catchments with woodland cover less than 30% had CL non-exceedance and positive, high flow, ANC values, suggesting that this is a sensible threshold value for risk assessments of the effects of broadleaf woodland expansion, as recommended by the Forests & Water Guidelines to protect acid-sensitive freshwater biota. However, limitations were identified in the critical loads methodology for assessing the risk of acidification in catchments subject to high seasalt deposition.

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References

Alexander, C.E., Cresser, M.S., 1995. An assessment of the possible impact of expansion of native woodland cover on the chemistry of Scottish freshwaters. Forest Ecology and Management 73, 1-27.

Barton, D., Gammack, S.M., Billett, M.F., Cresser, M.S., 1999. Sulphate adsorption and acidification of Calluna heathland and Scots pine forest podzol soils in north-east Scotland. Forest Ecology and Management 114, 151-164.

Battarbee, R.W., 1992. Critical loads and acid deposition for UK freshwaters. Environmental Change Research Centre Research Paper No.5, University College London, London.

BGS, 1995. Digital Map of Solid and Quaternary Geology; scale 1:625 000. British Geological Survey.

Curtis, C., Evans, C.D., Helliwell, R., Monteith, D.T., 2005. Nitrate leaching as a confounding factor in chemical recovery from acidification in UK upland waters. Environmental Pollution 137, 73-82.

Davies, J.J.L., Jenkins, A., Monteith, D.T., Evans, C.D., Cooper, D.M., 2005. Trends in surface water chemistry of acidified UK Freshwaters, 1988-2002. Environmental Pollution 137, 27-39.

ECRC, 2001. Acidification of freshwaters: the role of nitrogen and the prospects of recovery. Environmental Change Research Centre Report No. 79, University College London, London.

Evans, C.D., Monteith, D.T., Beaumont, B., Flower, R., Winterbottom, J., 2000. Site summaries, in: Monteith, D.T., Evans, C.D. (Eds.), UK Acid Waters Monitoring Network: 10 Year Report. Analysis and Interpretation of Results, April 1988-March 1998. ENSIS Publishing, London, pp. 37-268.

Forestry Commission, 2003. Forests & Water Guidelines, fourth ed. Forestry Commission, Edinburgh.

Fowler, D., Cape, J.N., Unsworth, M.H., 1989. Deposition of atmospheric pollutants on forests. Philosophical Transactions of the Royal Society of London B234, 247-265.

Fowler, D., Smith, R.I., Muller, J.B., Hayman, G., Vincent, K.J., 2005. Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. Environmental Pollution 137, 15-25.

Gagkas, Z., 2007. Effects of Broadleaf Woodland Cover on Streamwater Chemistry and Risk Assessments of Streamwater Acidification in Acid-sensitive Catchments in the UK, PhD Thesis, The University of Edinburgh.

Harriman, R., Morrison, B.R.S., Caines, L.A., Collen, P., Watt, A.W., 1987. Long-term changes in fish populations of acid streams and lochs in Galloway, south west Scotland. Water, Air and Soil Pollution 32, 89-112.

Harriman, R., Bridcut, E.E., Anderson, H., 1995. The relationship between salmonid fish densities and critical ANC at exceeded and non-exceeded stream sites in Scotland. Water, Air and Soil Pollution 85, 2455-2460.

Harriman, R., Watt, A.W., Christie, A.E.G., Collen, P., Moore, D.W., McCartney, A.G., Taylor, E.M., Watson, J., 2001. Interpretation of trends in acidic deposition and surface water chemistry in Scotland during the past three decades. Hydrology and Earth System Sciences 5, 407-420.

Henriksen, A., Dickson, W., Brakke, D.F., 1986. Critical loads for Sulphur and Nitrogen. Nordic Council of Ministers, Copenhagen, Denmark.

IUSS Working Group WRB, 2006. World Reference Base for Soil Resources, second ed. World Soil Resources Reports No. 103, FAO, Rome, Italy.

Jenkins, A., Cullen, J.M., 2001. An assessment of the potential impact of the Gothenburg Protocol on surface water chemistry using the dynamic MAGIC model at sensitive sites in the UK. Hydrology and Earth System Sciences 5, 529-541.

Lange, H., Solberg, S., Clarke, N., 2006. Aluminium dynamics in forest soil waters in Norway. Science of the Total Environment 367, 942-957.

Larssen, T., Holme, J., 2006. Afforestation, seasalt episodes and acidification - A paired catchment study in western Norway. Environmental Pollution 139, 440-450.

MISR, 1981. Digital Soil Map of Scotland; scale 1:250 000. Macaulay Institute for Soil Research.

Neal, C., 2001. Alkalinity measurements within natural waters: towards a standardised approach. The Science of the Total Environment 265, 99-113.

NEGTAP, 2001. Transboundary air pollution: acidification, eutrophication and ground-level ozone. CEH, Edinburgh.

Nisbet, T.R., Fowler, D., Smith, R.I., 1995. An investigation of the impact of afforestation on stream-water chemistry in the Loch Dee catchment, SW Scotland. Environmental Pollution 90, 111-120.

NSRI, 1984. National Soil Map of England and Wales; scale 1:250 000. National Soil Resources Institute, Cranfield University.

Ormerod, S.J., Donald, A.P., Brown, S.J., 1989. The influence of plantation forestry on the pH and aluminium concentration of upland Welsh streams: a re-examination. Environmental Pollution 62, 47-62.

Robertson, S.M.C., Hornung, M., Kennedy, V.H., 2000. Water chemistry of throughfall and soil water under four tree species at Gisburn, northwest England, before and after felling. Forest Ecology and Management 129, 101-117.

Rollinson, T., 2000. The UK policy context, in: Humphrey, J., Newton, A., Latham, J., Gray, H., Kirby, K., Poulsom, E., Quine, C. (Eds.), Proceedings of the Conference on the Restoration of Wooded Landscapes. Forestry Commission, Heriot-Watt University, Edinburgh, pp. 3-7.

Singles, R., Sutton, M.A., Weston, K.J., 1998. A multi-layer model to describe the atmospheric transport and deposition of ammonia in Great Britain. Atmospheric Environment 32, 393-399.

Stevens, P.A., Norris, D.A., Sparks, T.H., Hodgson, A.L., 1994. The impacts of atmospheric N inputs on throughfall, soil and stream water interactions for different aged forest and moorland catchments in Wales. Water, Air, and Soil Pollution 73, 297-317.

Stevens, P.A., Ormerod, S.J., Reynolds, B., 1997. Final Report of the Acid Waters Survey for Wales. Institute of Terrestrial Ecology, Bangor, Gwynedd, UK.

UBA, 2004. Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends. Report for the UNECE Convention on Long-Range Transboundary Air Pollution, Federal Environment Agency (Umweltbundesant), Berlin, Germany.

UK National Focal Centre, 2004. Update to the status of UK critical loads, critical loads methods, data & maps, CEH, Monks Wood.

Verburg, P.S.J., Johnson, D.W., Harrison, R., 2001. Long-term nutrient cycling patterns in Douglas-fir and red alder stands: a simulation study. Forest Ecology and Management 145, 203-217.

Tables

Table 1

Characteristics of the study catchments in Glen Arnisdale (GA), Loch Katrine (LK), Ullswater (UL), Yarner Wood (YAR) and Narrator Brook (NAR). GACON, LKCON, ULCON and NAR are control catchments for these sites (see text for explanation). Main soil types of area (after IUSS Working Group WRB, 2006). Key for cover of main soils: PZ=podzols, GL=gleysols and LP=leptosols. Critical load exceedance is from the provisional map for UK freshwaters.

Area	Geology of area	Main soil types of area	Catchment	Broadleaf woodland cover (%)	Catchment area (ha)	Mean (min-max) altitude (m)	Mean slope (º)	Cover of main soils (%)	Critical load exceedance class (keq $ha^{-1}yr^{-1}$)
Glen Arnisdale, north-west Scotland	Schists and gneisses of the Moine group	Histic podzols, histic gleysols, sapric histosols	GA1	27.3	66.0	444 (84-640)	29	PZ (53) GL (17)	0.0-0.2
			GA2	24.9	16.9	428 (53-611)	28	PZ (55) GL (19)	0.0-0.2
			GA3	20.3	53.5	338 (40-600)	29	PZ (37) GL (31)	0.0-0.2
			GACON	0.00	35.6	272 (9-489)	26	PZ (33) GL (32)	0.0-0.2
Loch Katrine,	Dalradian schists, grits	Osteinic albic folic and	LK1	29.0	103	412 (128-683)	26	PZ (90) GL (2)	0.5-1

southern Highlands, Scotland	and shales	histic podzols	LK2	16.3	132	461 (139-763)	23	PZ (81) GL (1)	0.5-1
			LK3	19.7	20.9	367 (185-556)	24	PZ (93) GL (7)	0.5-1
			LK4	10.3	39.6	502 (182-726)	26	PZ (89) GL (4)	0.5-1
			LKCON	0.00	47.6	407 (134-681)	24	PZ (91) GL (5)	0.5-1
Ullswater, north-west England	Ordovician slates and silicic tuffs	Histic gleysols, leptosols	UL1	53.4	8.56	306 (204-401)	9	GL (100)	Not exceeded adjacent square
			UL2	78.7	17.0	265 (176-386)	10	GL (97) LP (3)	Not exceeded adjacent square
			ULCON	0.00	8.99	313 (187-462)	22	LP (70) PZ (15) GL (15)	Not exceeded adjacent square
Devon, south-west England	Upper Carboniferous sandstones and slates	Histic stagnic podzols, haplic dystric cambisols	YAR	49.9	134	272 (108-411)	11	PZ (100)	0.2-0.5
	Granite		NAR	2.00	255	366 (255-456)	18	PZ (67) GL (33)	0.2-0.5

Table 2

Mean concentrations of Gran alkalinity, Ca, Na, Cl, marine and non-marine sulphate (xSO_4), NO_3, calculated ANC (all μeq l^{-1}), and Al (μmol l^{-1}) and Na:Cl ratio (of mean concentrations) in streamwater sampled at high flow in the study catchments. Figures in parentheses are min and max values. Catchment acronyms are given in Table 1.

Catchment	No. samples	Alkalinity	Ca	Na	Cl	Na:Cl ratio	Marine SO_4	xSO_4	NO_3	Al	ANC
GA1	2	33.9 (19.5-48.2)	116 (62.4-170)	338 (192-483)	534 (219-849)	0.63	57.3 (27.2-87.4)	16.8 (4.67-29.0)	3.72 (3.39-4.04)	1.76 (1.11-2.41)	-16.6 (-99.2-66.0)
GA2	2	8.80 (4.10-13.5)	91.5 (43.9-139)	397 (220-574)	563 (255-871)	0.71	58.8 (28.3-89.2)	10.9 (2.12-19.7)	3.42 (3.12-3.72)	1.89 (1.15-2.63)	10.0 (-22.6-42.6)
GA3	2	-13.4 (-20.5- -6.20)	68.2 (29.4-107)	429 (246-612)	648 (309-987)	0.66	64.5 (31.3-97.6)	12.6 (1.55-23.6)	3.47 (3.43-3.50)	1.96 (1.48-2.45)	-32.3 (-79.6-14.9)
GACON	2	24.4 (17.5-31.2)	121 (56.9-184)	466 (239-693)	703 (289-1116)	0.66	70.9 (38.7-103)	13.8 (8.91-18.7)	3.40 (3.25-3.54)	1.70 (1.04-2.37)	-13.2 (-67.3-41.0)
LK1	10	41.6 (15.2-97.5)	77.2 (51.9-93.3)	117 (99.6-143)	135 (95.1-205)	0.87	40.9 (31.3-51.7)	27.0 (12.4-38.2)	8.80 (4.11-13.7)	2.27 (1.22-3.71)	60.8 (-12.4-87.0)
LK2	10	-11.0 (-45.3-10.0)	44.3 (29.4-55.5)	109 (96.1-134)	120 (90.0-185)	0.91	34.4 (30.1-42.6)	22.0 (11.0-31.5)	6.59 (<0.30-12.1)	1.81 (0.78-2.48)	36.1 (-25.4-55.9)
LK3	10	2.51 (-28.9-26.2)	54.3 (36.9-69.4)	120 (101-151)	134 (91.4-201)	0.90	38.7 (30.2-46.2)	24.8 (12.0-33.1)	5.39 (<0.30-12.2)	1.40 (0.78-2.04)	40.4 (-18.0-55.6)
LK4	10	36.7 (17.4-61.0)	78.8 (56.9-94.8)	113 (94.8-136)	125 (91.2-187)	0.90	41.4 (33.4-49.8)	28.4 (15.2-37.3)	11.4 (5.49-16.8)	1.06 (0.70-1.82)	65.7 (0.41-94.9)
LKCON	9	31.7	71.1	114	118	0.97	39.5	27.3	7.09	0.79	74.8

		(-12.2-72.8)	(50.4-82.8)	(97.4-138)	(93.2-149)		(34.0-45.2)	(18.7-33.8)	(2.16-13.4)	(0.22-1.48)	(54.6-92.8)
UL1	5	-35.3 (-64.7- -1.44)	83.8 (57.2-119)	232 (193-268)	281 (191-336)	0.83	97.8 (76.0-123)	68.9 (47.5-88.6)	107 (12.2-179)	3.27 (2.08-4.04)	-76.1 (-181--19.5))
UL2	5	278 (171-385)	248 (135-347)	296 (222-357)	278 (235-312)	1.06	101 (91.5-116)	72.4 (60.8-83.3)	106 (30.3-169)	1.44 (0.59-2.37)	248 (100-290)
ULCON	5	141 (120-162)	143 (125-165)	175 (132-212)	156 (56.0-233)	1.12	83.9 (39.6-123)	67.9 (33.9-98.7)	4.97 (<0.30-8.44)	0.57 (0.52-0.63)	188 (72.4-197)
YAR	8	15.7 (-33.7-37.9)	42.5 (25.9-58.9)	279 (253-314)	334 (279-451)	0.84	80.0 (72.1-92.0)	45.6 (42.1-50.0)	41.4 (32.3-47.4)	2.46 (0.85-4.71)	-32.9 (-156-23.3)
NAR	3	15.1 (11.4-22.0)	31.1 (30.4-32.4)	210 (209-213)	250 (243-259)	0.84	83.3 (77.0-93.7)	57.5 (51.5-68.5)	7.85 (3.57-12.9)	1.87 (1.48-2.26)	-19.2 (-31.0-0.99)

Table 3

Correlation (Spearman's rank) matrix of r_s-values of mean streamwater high flow concentrations and selected catchment characteristics for the 14 study catchments. *P<0.05, **P<0.01, ***P<0.001.

	Gran alkalinity	Ca	Mg	Na	K	Cl	SO_4	NO_3	Al	% woodland cover	% gleysols	% podzols	Distance coast
Gran alkalinity	1.00												
Ca	*0.54	1.00											
Mg	0.15	**0.63	1.00										
Na	-0.13	0.38	***0.86	1.00									
K	-0.33	0.03	**0.63	***0.87	1.00								
Cl	-0.20	0.31	**0.79	***0.97	***0.86	1.00							
SO_4	0.17	0.41	**0.72	*0.53	0.30	*0.52	1.00						
NO_3	0.15	-0.17	-0.28	-0.44	-0.39	-0.42	0.28	1.00					
Al	*-0.53	-0.35	0.05	0.32	*0.48	*0.46	0.20	0.23	1.00				
% woodland cover	-0.07	0.08	0.18	0.25	0.19	0.28	0.29	*0.51	**0.64	1.00			
% gleysols	-0.07	**0.74	**0.72	*0.61	0.38	*0.53	0.44	-0.19	-0.01	0.25	1.00		
% podzols	-0.10	**-0.81	**-0.67	-0.43	-0.18	-0.40	*-0.51	0.10	0.06	-0.20	***-0.87	1.00	
Distance coast	-0.19	-0.23	**-0.76	**-0.80	***-0.90	***-0.90	*-0.48	*0.57	-0.19	-0.05	-0.39	0.29	1.00

Figure Legends

Fig. 1. Critical load exceedance squares (10 km x 10 km) of acidity (keq H ha^{-1} yr^{-1}) for freshwaters in the UK by non-marine S and N deposition for 1995-97 (Forestry Commission, 2003) and location of study catchments in Scotland and England.

Fig. 2. Association between catchment percentage broadleaf woodland cover and mean streamwater high flow (a) nitrate concentrations, (b) aluminium concentrations and (c) nitrate index values, NO_3:($x SO_4$ + NO_3) expressed in μeq l^{-1}. Catchment acronyms are given in Table 1.

Fig. 3. CL and CL exceedance values calculated with the SSWC model using modelled deposition data for 1995-97 and 2002 (generated by the FRAME model). Negative values indicate non-exceedance. Catchment acronyms are given in Table 1.

Figure 1

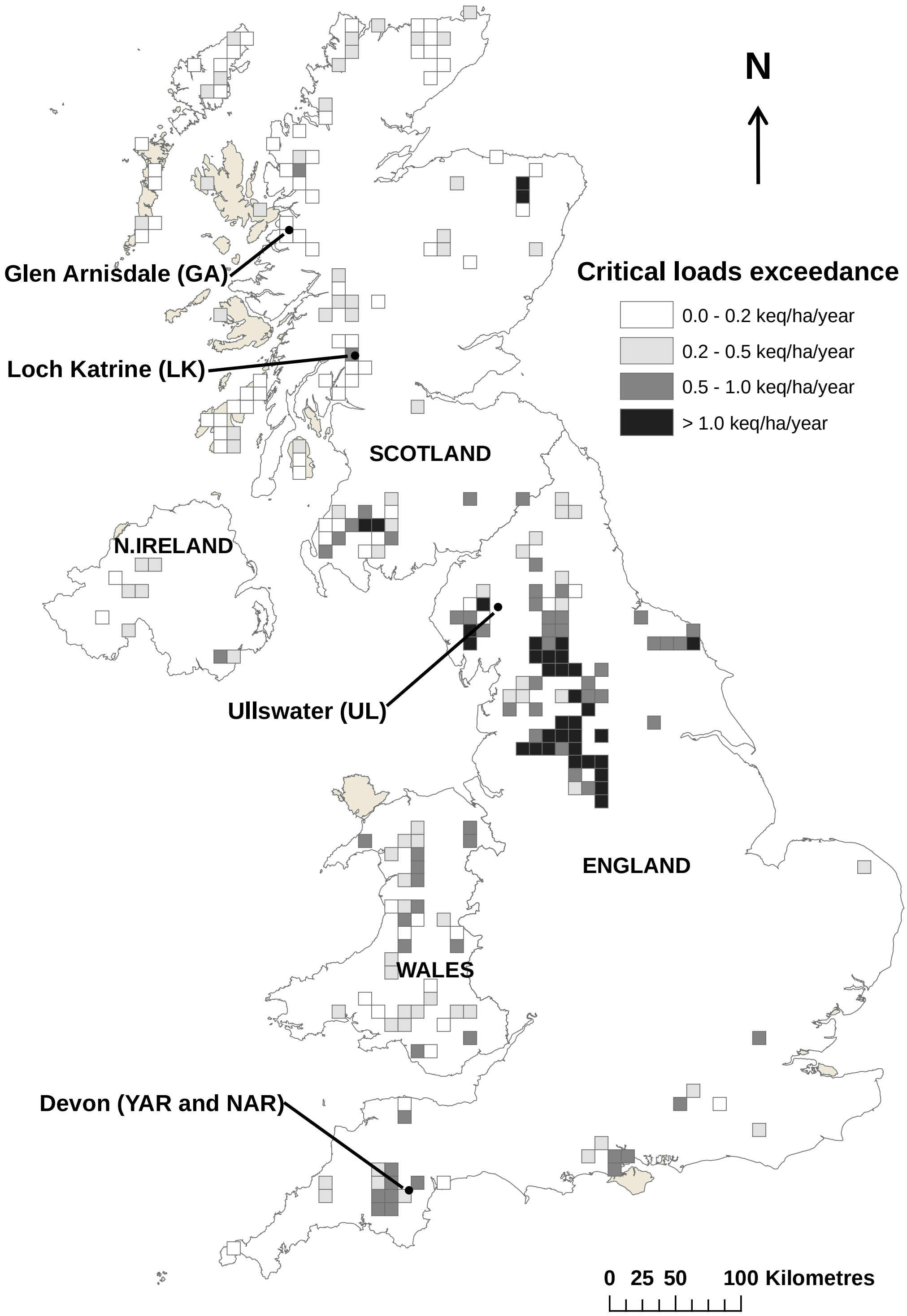

N
Critical loads exceedance
0.0 - 0.2 keq/ha/year
0.2 - 0.5 keq/ha/year
0.5 - 1.0 keq/ha/year
> 1.0 keq/ha/year
Glen Arnisdale (GA)
Loch Katrine (LK)
SCOTLAND
N.IRELAND
Ullswater (UL)
ENGLAND
WALES
Devon (YAR and NAR)
0 25 50 100 Kilometres

Figure 2

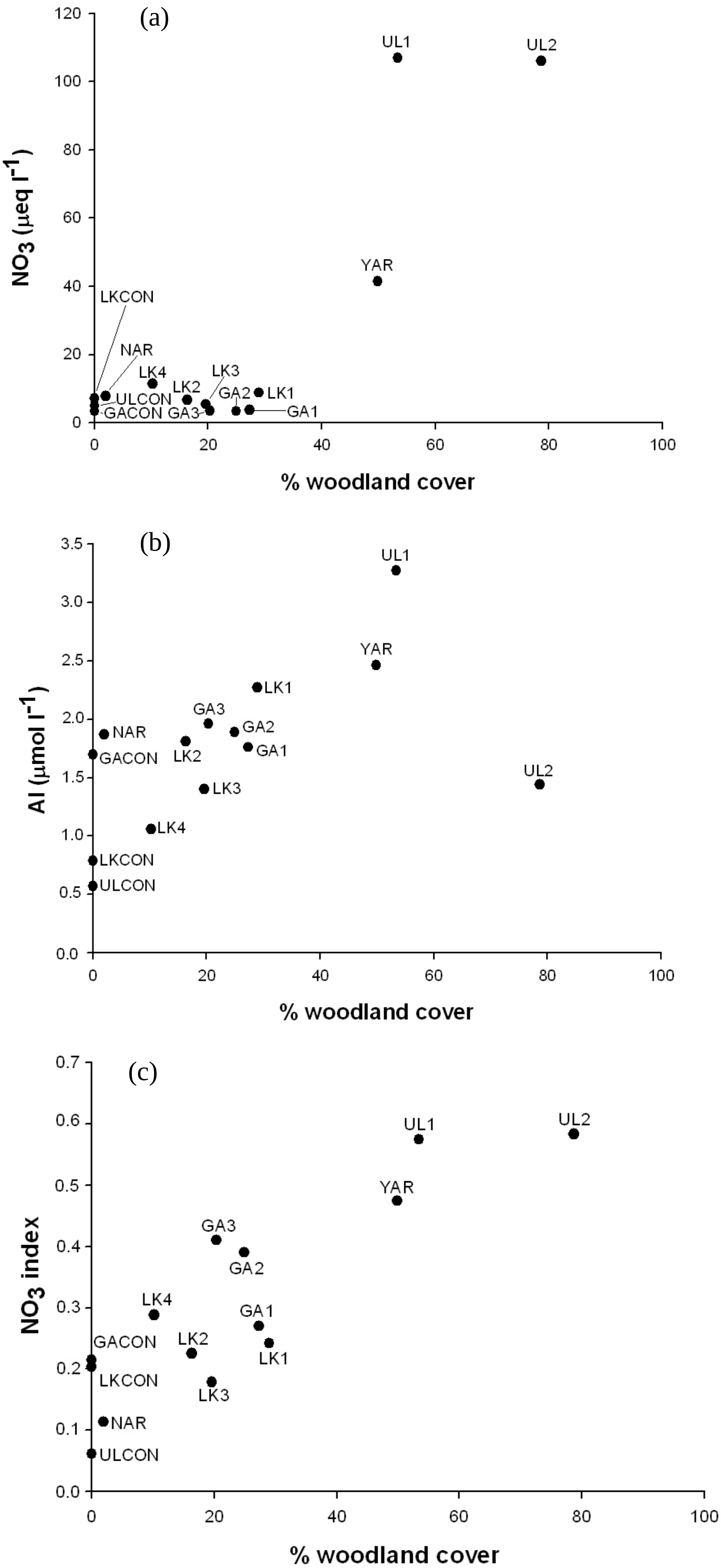
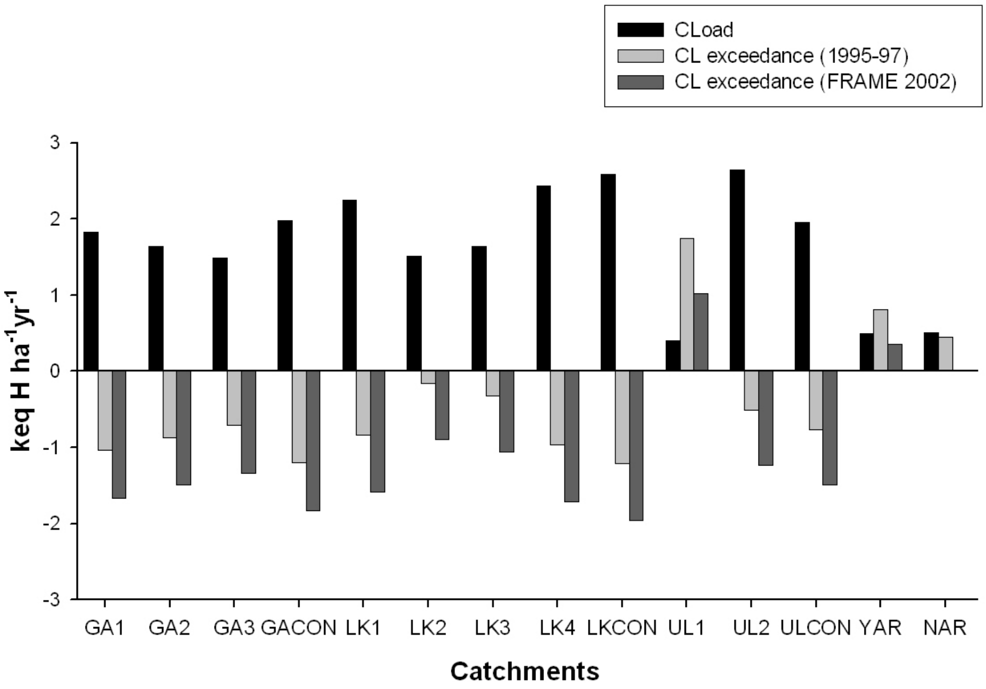

(a)
NO3 (μeq l-1)
0
20
40
60
80
100
120
UL1
UL2
YAR
LKCON
NAR
LK4
LK3
LK2
GA2
LK1
ULCON
GACON
GA3
GA1
% woodland cover
0
20
40
60
80
100
(b)
Al (μmol l-1)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
UL1
YAR
LK1
GA3
NAR
GA2
GACON
LK2
GA1
UL2
LK3
LK4
LKCON
ULCON
% woodland cover
0
20
40
60
80
100
(c)
NO3 index
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
UL1
UL2
YAR
GA3
GA2
LK4
GA1
GACON
LK2
LK1
LKCON
LK3
NAR
ULCON
% woodland cover
0
20
40
60
80
100

Figure 3



CLoad
CL exceedance (1995-97)
CL exceedance (FRAME 2002)
3
2
1
0
-1
-2
-3
keq H ha-1yr-1
GA1 GA2 GA3 GACON LK1 LK2 LK3 LK4 LKCON UL1 UL2 ULCON YAR NAR
Catchments